

Editorial on Ring-Opening Reactions of Epoxides

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DESCRIPTION

Other anhydrous acids (HX) can also open epoxides to generate a trans halohydrin. When both epoxide carbons are primary or secondary, the halogen anion attacks the less substituted carbon, resulting in an SN2 reaction.

Ring-opening polymerization (ROP) is a type of chain-growth polymerization in which the polymer chain's terminus attacks cyclic monomers to generate a longer polymer in polymer chemistry. The relief of bond-angle strain often drives the ring-opening of cyclic monomers.

Because substantial ring strain is eased when the ring opens upon nucleophilic attack, the carbons in an epoxide group are particularly reactive electrophiles. Epoxides are typically produced by the oxidation of an alkene in the laboratory and in the cell.

Epoxides are oxygen-containing three-membered rings. They have a high ring tension, which accounts for their reactivity to nucleophiles despite the fact that they lack a suitable leaving group. Because the angle between the carbons is 60° instead of 109.5°, which is what it should be for sp³-hybridized tetrahedral atoms, the ring strain is caused.

Using cyclopropane as an example, we can see this. Because the hydrogens are virtually permanently shadowed due to the locked sigma bonds between the carbons, three-membered rings have a torsional strain in addition to the ring strain.

Using strong nucleophiles to open epoxide rings

The SN2 mechanism is used in epoxide ring-opening reactions,

using the epoxide's oxygen as the leaving group. Because the result has an alkoxy group, it requires an aqueous or mild acidic work-up to yield neutral species.

SN1 vs. SN2, region selectivity, and stereo selectivity in epoxide ring-opening reactions

The non-enzymatic ring-opening reactions of epoxides give us a good overview of a lot of the principles we've covered so far in this chapter. Depending on the type of the epoxide and the reaction circumstances, ring-opening reactions can happen via SN2 or SN1 processes.

The structure of the result will differ depending on whether process dominates if the epoxide is asymmetric. When an asymmetric epoxide is solvated in basic methanol, an SN2 mechanism opens the rings, and the less substituted carbon becomes the target of nucleophilic attack, resulting in product B.

When solvolysis occurs in acidic methanol, however, the reaction follows an SN1 mechanism, with the more substituted carbon being the target of attack. As a result, product A takes the lead.

Both of these reactions are region selective in nature. Two (or more) separate constitutional isomers are feasible results in a region selective process, but one is generated preferentially (or sometimes exclusively).

Let's start with the most basic instance, the SN2. Because there is no acid available to protonate the oxygen prior to ring opening, the leaving group is an alkoxide anion. Because an alkoxide is a poor leaving group, the ring is unlikely to open without the nucleophile's help.

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